

CLAIMS

1. Process for preparing, by electrochemical reduction, a carbon-containing material whose surface is modified with organic groups, in particular functionalized organic groups, this process comprising placing the carbon-containing material in contact with an organic diazonium salt in solvent, optionally in the presence of an electrolyte, and negative polarization of the carbon-containing material relative to an anode which is also in contact with the solution of the organic diazonium salt or in contact with an electrolytic solution which is separate from the solution of the said salt, the said process being characterized in that the electrochemical reduction is carried out on an organic diazonium salt in protic solvent in acidic medium.

2. Process according to Claim 1, characterized in that the diazonium salt corresponds to the formula:



in which:

Ar is a C<sub>6</sub>-C<sub>14</sub> aromatic residue optionally functionalized with one or more substituents or a heteroaromatic residue of 5 to 14 atoms, optionally functionalized with one or more substituents, comprising one or more hetero atoms chosen from oxygen, nitrogen, sulphur and phosphorus,

X<sup>-</sup> is an anion.

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3. Process according to Claim 2, characterized in that the substituents are chosen from the group consisting of:

- linear or branched aliphatic radicals optionally comprising one or more double or triple bond(s), optionally substituted with carboxyl, NO<sub>2</sub>, disubstituted protected amino, monosubstituted protected amino, cyano, diazonium, alkoxy, alkoxycarbonyl, alkylcarbonyloxy or optionally fluorinated vinyl radicals or halogen atoms,
- aryl radicals optionally substituted with carboxyl, NO<sub>2</sub>, disubstituted protected amino, monosubstituted protected amino, cyano, diazonium, alkoxy, alkoxycarbonyl, alkylcarbonyloxy or optionally fluorinated vinyl radicals or halogen atoms,
- carboxyl, NO<sub>2</sub>, disubstituted protected amino, monosubstituted protected amino, cyano, diazonium, alkoxy, alkoxycarbonyl, alkylcarbonyloxy or optionally fluorinated vinyl radicals or halogen atoms.

4. Process according to Claim 3, characterized in that the said organic group is functionalized with one or more substituents capable of reacting directly with a substrate or with one or more precursor substituents which, after conversion, are capable of reacting with a substrate, the said substrate being chosen from the group consisting of organic resins, biological molecules, chemical molecules and complexing agents.

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5. Process according to Claim 4,  
characterized in that the substituents capable of  
reacting directly with an organic resin are chosen from  
the group consisting of  $-(CH_2)_n-COOH$ ,  $-(CH_2)_n-CH_2-OH$  and  
5  $(CH_2)_n-NH_2$  groups,  $n$  being an integer between 0 and 10,  
and in that the precursor substituents capable of  
reacting, after conversion, with an organic resin are  
chosen from the group consisting of  $NO_2$ ,  $N_2^+$ ,  $(CH_2)_n-CN$ ,  
 $(CH_2)_n-CHO$  and  $(CH_2)_n-COOPr$  groups,  $Pr$  being a protecting  
10 group, and  $(CH_2)_n-NHP'r$ ,  $(CH_2)_n-N(P'r)_2$  and  $(CH_2)_n-N=P''r$   
groups,  $P'r$  and  $P''r$  being protecting groups and  $n$  being  
an integer between 0 and 10.

6. Process according to Claim 4,  
characterized in that the substituents capable of  
15 reacting directly with a biological molecule are chosen  
from the group consisting of  $(CH_2)_n-COOH$  and  $(CH_2)_n-NH_2$   
groups,  $n$  being an integer between 0 and 10, and in  
that the precursor substituents capable of reacting,  
after conversion, with a biological molecule are chosen  
20 from the group consisting of  $NO_2$ ,  $N_2^+$ ,  $(CH_2)_n-CN$ ,  $(CH_2)_n-$   
 $CHO$  and  $(CH_2)_n-COOPr$  groups,  $Pr$  being a protecting group  
and  $n$  being an integer between 0 and 10.

7. Process according to Claim 4,  
characterized in that the substituents capable of  
25 reacting directly with functional organic molecules are  
chosen from the group consisting of  $NO_2$ ,  $(CH_2)_n-CONH_2$ ,  
 $(CH_2)_n-CN$ ,  $(CH_2)_n-CHO$ ,  $(CH_2)_n-COOH$ ,  $(CH_2)_n-CH_2OH$  and  $(CH_2)_n-$   
 $NH_2$  groups,  $n$  being an integer between 0 and 10, and

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SO<sub>2</sub>H, SO<sub>3</sub>H, SO<sub>2</sub>R and SO<sub>3</sub>R groups, R being an aliphatic or aromatic carbon-based chain of 1 to 20 carbon atoms and in that the precursor substituents capable of reacting, after conversion, with functional organic molecules are  
5 chosen from the group consisting of NO<sub>2</sub>, (CH<sub>2</sub>)<sub>n</sub>-CONH<sub>2</sub> and (CH<sub>2</sub>)<sub>n</sub>-COOPr groups, Pr being a protecting group, and (CH<sub>2</sub>)<sub>n</sub>-NHP'r, (CH<sub>2</sub>)<sub>n</sub>-N(P'r)<sub>2</sub> and (CH<sub>2</sub>)<sub>n</sub>-N=P''r groups, P'r and P''r being protecting groups, and (CH<sub>2</sub>)<sub>n</sub>-CN, (CH<sub>2</sub>)<sub>n</sub>-CHO, (CH<sub>2</sub>)<sub>n</sub>-COOH and (CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>OH groups, n being an  
10 integer between 0 and 10, and SO<sub>2</sub>Pr and SO<sub>3</sub>Pr groups, Pr being a protecting group chosen from the meanings of R.

8. Process according to Claim 1, characterized in that the protic solvent is chosen from the group consisting of water, methanol and ethanol or  
15 mixtures thereof.

9. Process according to Claim 8, characterized in that the protic solvent is in a mixture with an aprotic solvent, it being understood that the mixture has the characteristics of an aprotic  
20 solvent.

10. Process according to Claim 1, characterized in that the acid is chosen from sulphuric acid, hydrochloric acid, nitric acid, nitrous acid, phosphoric acid and tetrafluoroboric acid.

25 11. Process according to one of Claims 1 to 10, characterized in that the pH of the solution is less than 2.

12. Process according to Claim 1,

characterized in that the reduction is carried out by repetitive cyclic voltammetry in a potential range in which the diazonium salts are reduced or by electrolysis at a potential which is more negative than the reduction potential of the diazonium salt.

13. Process according to Claim 1, characterized in that the diazonium salt concentration is between  $10^{-3}$  and  $10^{-1}$  mol/l.

10 14. Process for the electrochemical production of a carbon-containing material whose surface is modified with aromatic amino groups, according to one of Claims 1 to 13, characterized in that the aromatic diazonium salt is substituted with a nitro radical and in that the electrochemical reduction is maintained up to the reduction of the nitro radical into an amino radical.

15 15. Process according to one of Claims 1 to 14, characterized in that the carbon-containing material is in the form of fibres, powder, felt, fabric or carbon/carbon composite.

20 16. Process according to one of the preceding claims, characterized in that the modified carbon-containing materials are subjected to a subsequent conversion of the functional substituents.

25 17. Carbon-containing material modified at the surface with optionally functionalized organic groups, which can be obtained by the process according to one of Claims 1 to 16.

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18. Material according to Claim 17,  
characterized in that it consists of carbon fibres or  
of a carbon-containing material in the form of powder  
or of a carbon-containing material in the form of felt,  
5 fabric, beads or carbon/carbon composite.

19. Composite material formed from an  
organic resin reinforced with fibres of carbon-  
containing material according to Claim 18, the surface  
of which has been modified with organic groups  
10 functionalized with substituents capable of reacting  
directly, or after conversion, with an organic resin.

20. Application of the materials according  
to Claim 17, at the surface of which are bound organic  
groups capable of reacting with a biological molecule  
15 of interest, for carrying out biological reactions.

21. Application of the materials according  
to Claim 17, at the surface of which are bound organic  
groups capable of reacting with a metal cation, with a  
functionalized organic molecule or a complexing agent,  
20 for carrying out such reactions.

22. Use of the process according to Claims 1  
to 16, to make a combinatorial chemistry library of  
organic compounds.

23. Application of the materials according  
25 to Claim 17, at the surface of which are bound organic  
groups capable of reacting with functional organic  
molecules, to make a combinatorial chemistry library.

24. Application according to Claim 23, of

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materials, at the surface of which are bound organic groups, characterized in that the said organic groups undergo one or more chemical and/or electrochemical conversions and are then cleaved from the carbon-  
5 containing material.

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